COHERENCE RELAXATION DURING DIFFUSION OF RESONANCE RADIATION

M. I. D'YAKONOV and V. I. PEREL'

A. F. Ioffe Physico-technical Institute, Academy of Sciences, U.S.S.R.

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We derive equations describing the change in time of the off-diagonal (with respect of the magnetic quantum numbers) matrix elements of the density matrix of excited gas atoms when there is diffusion of the radiation. We show that when there is complete capture of the radiation, there are two relaxation times for linear and for circular polarization, respectively. We give expressions for them. We obtain approximate expressions for these relaxation times and also for the decay time of the excited state when the capture is incomplete. The pressure dependence found here agrees with experimental data.

1. STATEMENT OF THE PROBLEM

A number of phenomena connected with the scattering of resonance radiation makes it possible to determine the natural line width under conditions when the Doppler width is appreciably larger than the natural one [1-4]. A typical effect of this kind is the Hanle effect which consists of the following. A gas in a magnetic field H is irradiated by light, polarized at right angles to the field. The scattered radiation is observed at right angles to the field and to the exciting beam. When the magnetic field is increased the degree of polarization P of the scattered light tends to zero according to the law

$$P = P_0\gamma^2 / (\gamma^2 + 4\omega_H^2). \qquad (1)$$

Here P_0 is the degree of polarization when there is no magnetic field, $\omega_H = \mu_0 gH$, μ_0 is the Bohr magneton, g the Landé factor, and γ the natural width of the level.

It turns out that when the gas pressure is increased the magnetic depolarization line (and also the double resonance line) narrows so that the quantity γ determined from these experiments turns out to be less than the natural line width [5,6]. The reason is the capture of the resonance radiation. Let us, for instance, consider the case when the lower state has a total angular momentum $j_0 = 0$, and the upper state $j_1 = 1$. Under conditions of complete capture each light quantum emitted by one atom is absorbed by another atom. The decay time of an excited state is thus infinite.

We can represent an atom as a set of three mutually perpendicular dipoles. One can show easily, using the diagram of the directivity of a dipole, that the energy of the radiation of a dipole oriented, for instance, along the z axis, is distributed over the components of the electrical field in such a way that $E_z^2 : E_x^2 : E_y^2 = 8:1:1$. We get thus for the energy I_z of the oscillations of the z-dipole the equation

$$dI_z / dt = -\gamma I_z + {}^4/_5\gamma I_z + {}^1/_{10}\gamma I_x + {}^1/_{10}\gamma I_y.$$

We now introduce the quantity $I = I_z - {}^1/_3(I_x + I_y + I_z)$ characterizing the preferential polarization of the atoms in the z-direction. It is clear that we have for this quantity $dI/dt = -3\gamma I/10$. The time $(3\gamma/10)^{-1}$ can be called the decay time of the plane polarization for the example considered. It is just this quantity which will determine the line width in magnetic depolarization experiments, double resonance experiments, and so on. The papers by Barrat [7] were devoted to the calculation of the quantity which we called here the decay time of the plane polarization and which he called longitudinal coherence.

In the present paper we derive equations describing the change in time of the density matrix of an excited atom when the radiation is captured. These equations [Eq. (17)] are, in the case when the density matrix is diagonal, the same as the well-known radiation diffusion equation [8]. We show for the case of complete capture that the decay of the off-diagonal part of the density matrix (the coherence by Brossel's definition [9]) and the equalization of the population in the Zeeman sublevels takes place with two characteristic relaxation times [Eq. (31)]. One of them, $\gamma_{2\infty}^{-1}$ is in fact the decay time of the plane polarization, calculated by Barrat, the other one, $\gamma_{1\infty}^{-1}$ has the meaning of the decay of the magnetic moment (it can be called also the decay time of the circular polarization).

When the capture is incomplete (bounded volume of the medium) we can approximately introduce three relaxation times (Eq. (35)): two of them, γ_1^{-1} and γ_2^{-1}, have the same meaning as $\gamma_{1\infty}^{-1}$ and $\gamma_{2\infty}^{-1}$, and the third one, γ_0^{-1}, characterizes the decay of the excited state (for the case of complete capture $\gamma_{0\infty} = 0$).

The nature of the dependence of these times on the dimensions of the volume or the gas pressure differs strongly from the dependence found by Barrat. This is connected with the fact that Barrat approximated the velocity distribution of the atoms by a single-velocity distribution. In the problem of the diffusion of radiation such an approximation is inadmissable since it leads to a finite mean free path of the photon. Indeed, it is well known [8,10] that one can not introduce such a concept.

In the present paper we shall assume that the distance between the atoms is appreciably larger than the wavelength of the light and that the Doppler width of the emitted line is appreciably larger than the natural line width and the Zeeman splitting. On the other hand, we shall assume the hyperfine splitting of the upper and the lower level to be larger than the Doppler width so that we may consider only the transitions between two levels characterized by the values of the total angular momentum which we shall denote by j_0 and j_1. In the following we shall put $\hbar = c = 1$.

The Hamiltonian of the system has the form

$$\mathcal{H} = \mathcal{H}_a + \mathcal{H}_n + \mathcal{H}_{\text{ph}} + V_1 + V_2.$$

Here $\mathcal{H}_a$, $\mathcal{H}_n$, $\mathcal{H}_{\text{ph}}$ are, respectively, the Hamiltonians of the interacting excited atoms, the atoms in their ground state, and the photons:

$$\mathcal{H}_a = \sum_{\mathbf{p}m} (\varepsilon_{\mathbf{p}} + \omega_0)\, a_{\mathbf{p}m}^{+} a_{\mathbf{p}m},$$

$$\mathcal{H}_n = \sum_{\mathbf{p}\mu} \varepsilon_{\mathbf{p}} \alpha^{+}_{\mathbf{p}\mu} \alpha_{\mathbf{p}\mu}, \quad \mathcal{H}_{\text{ph}} = \sum_{\mathbf{q}\lambda} q b_{\mathbf{q}\lambda}^{+} a_{\mathbf{q}\lambda};$$

$\epsilon_{\mathbf{p}}$ is the kinetic energy of an atom with momentum $\mathbf{p}$; $\epsilon_{\mathbf{p}} = p^2/2M$; ω_0 is the excitation energy. The indices m number the Zeeman sublevels of the excited state and the indices μ those of the ground state; $\mathbf{q}$ is the wave vector of the photon; and λ its polarization. In the chosen system of units the magnitude of $\mathbf{q}$ is the same as the energy of a photon with wave vector $\mathbf{q}$; $a_{\mathbf{p}m}$, $\alpha_{\mathbf{p}\mu}$, and $b_{\mathbf{q}\lambda}$ are, respectively the annihilation operators of excited atoms, atoms in the ground state, and photons; V_1 is the interaction between the photons and the atoms:

$$V_1 = \frac{1}{\sqrt{V}} \sum_{\mathbf{p}\mathbf{q}\lambda m\mu} C_{\mathbf{q}\lambda}^{m\mu} b_{\mathbf{q}\lambda} a_{\mathbf{p}m}^{+} \alpha_{\mathbf{p}-\mathbf{q},\,\mu} + \text{c.c.};$$

$$C_{\mathbf{q}\lambda}^{m\mu} = \left(\frac{2\pi\omega_0^2}{q}\right)^{1/2} (\mathbf{e}_{\mathbf{q}\lambda} \mathbf{d}_{m\mu}). \tag{2}$$

$\mathbf{e}_{\mathbf{q}\lambda}$ is the polarization vector of the photon, $\mathbf{d}_{m\mu}$ the matrix element of the dipole moment of the atom, V_2 is the interaction of the atoms with the external field which causes the transition of the atom from the ground state into an excited state. The exciting agent may be either external radiation or electron impacts. We shall not use here an explicit form of V_2.

We do not include in the Hamiltonian the longitudinal part of the interaction between the atoms, which is connected with the Coulomb interaction of the electrons and nuclei. This interaction leads to exchange excitations under pair of collisions [11]. The frequency of such collisions is of the order of $n_0\lambda^3\gamma$ where n_0 is the concentration of atoms in their ground state and λ the wavelength of the light. Under the conditions considered here $n_0\lambda^3 \ll 1$ so that we can neglect this effect.

2. DERIVATION OF THE GENERALIZED EQUATION FOR RADIATION DIFFUSION

The density matrix ρ of the system satisfies the equation

$$i\partial\rho / \partial t = [\mathcal{H}, \rho],$$

which has the formal solution

$$\rho(t) = \exp\left(-i \int_0^t \mathcal{H}\, dt\right) \rho_0 \exp\left(i \int_0^t \mathcal{H}\, dt\right). \tag{3}$$

Here ρ_0 is the initial density matrix: $\rho_0 = \rho_n \rho_{ph} \rho_a$, where ρ_{ph} is the vacuum photon density matrix; ρ_a the density matrix of the excited atoms corresponding to a state where there are none; $\rho_n = \exp(-\beta\mathcal{H}_n)/\text{Tr}\exp(-\beta\mathcal{H}_n)$ is the equilibrium density matrix of the atoms in their ground state; β^{-1} the temperature of the gas.

We introduce the single-particle density matrix of the excited atoms:

$$f_{mm'}(\mathbf{p}, \boldsymbol{\varkappa}, t) = \text{Sp}\, \rho a^{+}_{\mathbf{p}-\boldsymbol{\varkappa}/2,\, m'} a_{\mathbf{p}+\boldsymbol{\varkappa}/2,\, m}. \tag{4}$$

The function

$$f_{mm}(\mathbf{p}, \mathbf{r}, t) = \frac{1}{(2\pi)^3} \int e^{i\boldsymbol{\varkappa}\mathbf{r}} f_{mm}(\mathbf{p}, \boldsymbol{\varkappa}, t)\, d^3\boldsymbol{\varkappa} \tag{5}$$

is the classical distribution function of the excited atoms in the level m. Substituting (3) in (4), we get

$$f_{mm'}(\mathbf{p}, \boldsymbol{\varkappa}, t) = \text{Sp}\, \rho_0 \exp\left(i \int_0^t \mathcal{H}\, dt\right) a^{+}_{\mathbf{p}-\boldsymbol{\varkappa}/2,\, m'} a_{\mathbf{p}+\boldsymbol{\varkappa}/2,\, m}$$

$$\times \exp\left(-i \int_0^t \mathcal{H}\, dt\right).$$

We use the identity

$$\exp\left(-i\int_0^t \mathcal{H}\,dt\right) = \exp(-i\mathcal{H}_0 t)\,T\exp\left(-i\int_0^t V(t')\,dt'\right),$$

$$V(t) = \exp(i\mathcal{H}_0 t)\,V\exp(-i\mathcal{H}_0 t);$$

$$\mathcal{H}_0 = \mathcal{H}_a + \mathcal{H}_{\rm ph} + \mathcal{H}_n; \qquad V = V_1 + V_2.$$

The expression for the single-particle density matrix can then be written in the form

$$f_{mm'}(\mathbf{p}, \varkappa, t) = \mathrm{Sp}\,\rho_0 T_C a^+_{\mathbf{p}-\varkappa/2,\,m'}(t)\,a_{\mathbf{p}+\varkappa/2,\,m}(t)$$

$$\times\exp\left(-i\int_C V(t')\,dt'\right).$$

Here T_C orders the operators along the contour C. The contour C goes from the point t = 0 to the point t (upper part) and then back to the point t = 0 (lower part). It is depicted in Fig. 1.

To evaluate the quantity $f_{mm'}(\mathbf{p}, \kappa, t)$ we can use the diagram technique developed by Konstantinov and one of the authors.[12] There is only one difference in that in our case there is no part of the contour C along the imaginary axis. To evaluate the quantity

$$f_{mm'}(\mathbf{p}, \varkappa, s) = \int_0^\infty e^{-st} f_{mm'}(\mathbf{p}, \varkappa, t)\,dt \tag{7}$$

we have the following rule. Dotted lines refer to atoms in their ground state. Irregular lines (i.e., lines going from "later" points on the contour to "earlier" ones) correspond to a factor

$$n_{p\mu} = \mathrm{Sp}\,\rho_n \alpha^+_{\mathbf{p}\mu}\alpha_{\mathbf{p}\mu} = \frac{8\pi^{3/2} n_0}{(2j_0+1)\,p_0^3}\exp\left(-\frac{p^2}{p_0^2}\right) \equiv \frac{n_p}{2j_0+1}. \tag{8}$$

Here n_0 is the concentration, $p_0 = \sqrt{2M/\beta}$ the thermal momentum, and $2j_0 + 1$ the degree of degeneracy of the lower level. Full drawn lines correspond to excited atoms, and wavy lines to photons. In the following we shall restrict ourselves to an approximation linear in the concentrations of the excited atoms and the photons. The solid and wavy lines can therefore only be regular ones. To all regular lines there corresponds a factor unity, since $\mathrm{Tr}\,\rho_n \alpha_{\mathbf{p}\mu}\alpha^+_{\mathbf{p}\mu} = 1 \pm n_{\mathbf{p}\mu} \approx 1$ when there is no degeneracy. The diagrams are

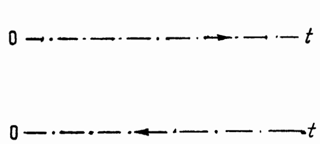

FIG. 1

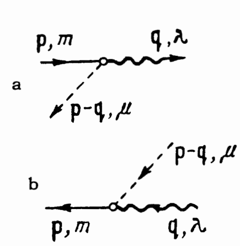

FIG. 2

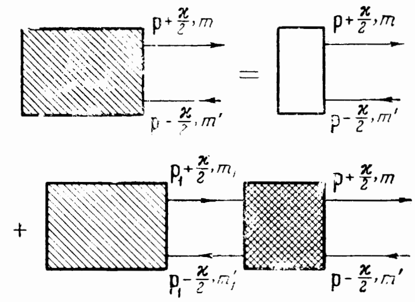

FIG. 3

then no longer dependent on whether the atoms are fermions or bosons.

Points such as the ones shown in Fig. 2 correspond to the interaction V_1. The point 2a (emission of a photon) corresponds to a factor $C^{m\mu *}_{\mathbf{q}\lambda}$. The point 2b (absorption of a photon) to a factor $C^{m\mu}_{\mathbf{q}\lambda}$. Moreover, to each point on the upper part of the contour corresponds a factor $-i$ and to a point on the lower part i. As in [12], a vertical section corresponds to factors $(s + i\Omega_{MN})^{-1}$, where Ω_{MN} is the difference in energy of the lines going through the section to the right and to the left. We sum over all momenta, polarizations, and sublevels corresponding to internal lines. For instance, the section of the diagram given in Fig. 4c corresponds to a factor

$$(-i)^2\frac{1}{V}\sum_{\mathbf{q}\lambda}\sum_{\mu}\frac{C^{m_1\mu *}_{\mathbf{q}+\varkappa/2,\,\lambda}\,C^{m\mu}_{\mathbf{q}+\varkappa/2,\,\lambda}}{s + i(\varepsilon_{\mathbf{p}-\mathbf{q}} - \varepsilon_{\mathbf{p}-\varkappa/2} + |\mathbf{q}+\varkappa/2| - \omega_0)}. \tag{9}$$

We can use for the function $f_{mm'}(\mathbf{p}, \kappa, s)$ the equation of Fig. 3:

$$f_{mm'}(\mathbf{p}, \varkappa, s) = F_{mm'}(\mathbf{p}, \varkappa, s)\,[s + i(\varepsilon_{\mathbf{p}+\varkappa/2} - \varepsilon_{\mathbf{p}-\varkappa/2})]^{-1}$$

$$+ \sum_{m_1 m_1' \mathbf{p}_1} f_{m_1 m_1'}(\mathbf{p}_1, \varkappa, s)\,W^{m_1 m_1'}_{mm'}(\mathbf{p}, \mathbf{p}_1; \varkappa, s)$$

$$\times\,[s + i(\varepsilon_{\mathbf{p}+\varkappa/2} - \varepsilon_{\mathbf{p}-\varkappa/2})]^{-1}. \tag{10}$$

Here $F_{mm'}(\mathbf{p}, \kappa, s)$ is the term describing the influence of the exciting external field. The doubly hatched square $W^{m_1 m_1'}_{mm'}(\mathbf{p}, \mathbf{p}_1; \kappa, s)$ is the sum of irreducible diagrams, i.e., diagrams which can

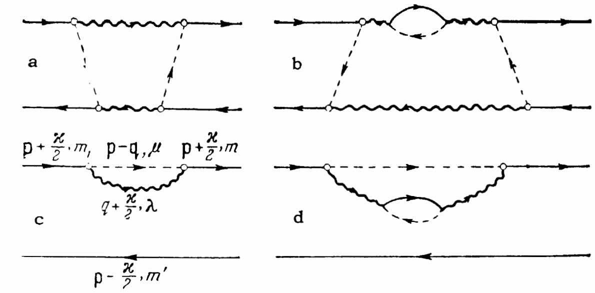

FIG. 4

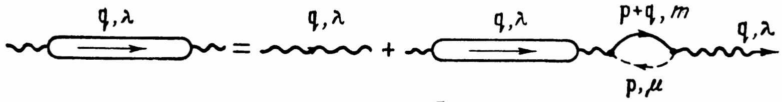

FIG. 5

not be cut into two by a section intersecting only two solid lines.

Some of the diagrams contained in W are given in Fig. 4. The diagram of Fig. 4c describes the decay of an excited state when emission is taken into account. We can neglect in Eq. (9) the quantities κ, s, and qp/M compared to q or ω_0. One must complete the diagram of Fig. 4c by a similar diagram in which the photon line occurs in the lower part of the contour. After calculations we then get

$$W_1 = -\delta_{mm_1}\delta_{m'm_1'}\delta_{\mathbf{pp}_1}\gamma, \quad \gamma = {}^4/_3\omega_0^3 d^2; \tag{11}$$

γ is the natural width of the excited state, $d^2 = \Sigma_\mu |d_{m\mu}|^2$.

The diagram of Fig. 4a describes the transition of atoms into an excited state, taking into account the absorption of a photon, emitted beforehand by another atom (diffusion of radiation). Diagram 4b takes into account the possibility that the photon is absorbed on its way from the first to the second atom. Diagram 4d describes the influence of the gas pressure on the natural width of the excited level. An estimate shows that it is small compared to diagram 4c if $n_0\lambda^3\gamma/\Delta\omega_D \ll 1$, where $\Delta\omega_D$ is the Doppler width of the line. Under the assumptions made here it turns out that diagrams such as 4a and 4b make the main contributions to W.

To sum all such diagrams we use a method similar to the one used in a paper by Konstantinov and one of the authors.[13] We introduce the photon Green function $D_{q\lambda}(t)$ which satisfies the equation depicted in Fig. 5. This function is easily evaluated by means of a Laplace transformation:

$$D_{\mathbf{q}\lambda}(\eta) \equiv \int_0^\infty e^{-\eta t} D_{\mathbf{q}\lambda}(t)\,dt = 1/[\eta + iq + \Gamma_{\mathbf{q}\lambda}(\eta)/2], \tag{12}$$

$$\Gamma_{\mathbf{q}\lambda}(\eta) = \frac{2}{V}\sum_{\mathbf{p}m\mu}\frac{n_p}{\eta + i(\varepsilon_{\mathbf{p}+\mathbf{q}} - \varepsilon_{\mathbf{p}} + \omega_0)}\frac{|C^{m\mu}_{\mathbf{q}\lambda}|^2}{2j_0+1}. \tag{13}$$

We also introduce the function

$$\widetilde{D}_{\mathbf{q}\lambda}(\eta) = \int_0^\infty e^{-\eta t} D^*_{\mathbf{q}\lambda}(t)\,dt$$

and the function $\widetilde{\Gamma}_{q\lambda}(\eta)$ corresponding to it. Using the fact that

$$D_{\mathbf{q}\lambda}(t) = \frac{1}{2\pi i}\int_{-i\infty+\sigma}^{i\infty+\sigma} e^{\eta t} D_{\mathbf{q}\lambda}(\eta)\,d\eta, \quad D_{\mathbf{q}\lambda}^*(t) = \frac{1}{2\pi i}\int_{-i\infty+\sigma}^{i\infty+\sigma} e^{\eta t}\widetilde{D}_{\mathbf{q}\lambda}(\eta)\,d\eta,$$

we can replace all photon lines by "fat" ones and each "fat" line corresponds to a factor $D_{q\lambda}(\eta)$ on the upper part of the contour and to $\widetilde{D}_{q\lambda}(\eta)$ on the lower part. The index λ of the functions D will be dropped in the following since they do, in fact, not depend on the polarization of the photon. When we write down the factors corresponding to a section, we must take the "fat" photon line directed to the right and assign to it an "energy" $i\eta$. We must integrate over all η as follows:

$$\frac{1}{2\pi i}\int_{-i\infty+\sigma}^{i\infty+\sigma} d\eta.$$

Note that the functions $D_q(\eta)$ and $\widetilde{D}_q(\eta)$ are analytical in the right half-plane.

The sum of all diagrams such as 4a and 4b takes the form given in Fig. 6. There are always four diagrams of the kind 6a (with different directions of the dotted lines), and two of the kind 6b. When evaluating the corresponding terms in W we shall neglect the quantities s and $\kappa \cdot v_p$ as compared to the Doppler line width $q \cdot v_p$ ($v_p = p/M$). This means that the characteristic time for a change in the density matrix f is large compared with the inverse Doppler line width and that the characteristic distance over which f changes is large compared with the wave length of the radiation. We then can obtain

$$W_2 = \frac{\gamma}{\omega_0}\frac{1}{V^2}\sum_{\mathbf{q}} n_{\mathbf{p}-\mathbf{q}} 2\pi\delta(\mathbf{qv}_p - \mathbf{qv}_{p_1})\int_{-i\infty}^{i\infty}\frac{d\eta}{2\pi i}\int_{-i\infty}^{i\infty}\frac{d\eta'}{2\pi i}$$

$$\times\frac{D_{\mathbf{q}+\varkappa/2}(\eta)}{s - i\omega_0 - i\mathbf{qv}_p - \eta}\,\frac{\widetilde{D}_{\mathbf{q}-\varkappa/2}(\eta')}{s + i\omega_0 + i\mathbf{qv}_p - \eta'}\,G^{m_1m_1'}_{mm'}; \tag{14}$$

$$G^{m_1m_1'}_{mm'}(\mathbf{q}) = \sum_{\substack{\mu\mu'\\ \lambda\lambda'}}(C^{m_1\mu'}_{\mathbf{q}\lambda})^*\,C^{m\mu}_{\mathbf{q}\lambda}C^{m_1'\mu'}_{\mathbf{q}\lambda'}(C^{m'\mu}_{\mathbf{q}\lambda'})^*\frac{1}{2j_0+1}\frac{\omega_0}{\gamma}.$$

We can calculate the integrals over η and η' by closing the contour of integration in the right half-plane and using the fact that the functions $D_q(\eta)$ are analytical in that half-plane. After this, the expression for W_2 becomes

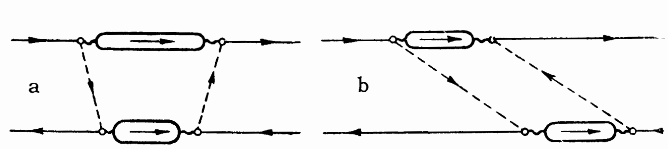

FIG. 6

$$W_2 = \frac{\gamma}{\omega_0}\frac{1}{V}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\, n_{\mathbf{p}-\mathbf{q}}\,\frac{1}{q}\, 2\pi\delta(\mathbf{kv}_p - \mathbf{kv}_{p_1})\, G_{mm'}^{m_1m_1'}(\mathbf{q})$$
$$\times[s - i\omega_0 - i\,\mathbf{qv}_p + i\,|\,\mathbf{q}+\boldsymbol{\varkappa}/2\,|$$
$$+\Gamma_{\mathbf{q}}(s - i\omega_0 - i\,\mathbf{qv}_p)/2]^{-1}[s + i\omega_0 + i\mathbf{qv}_p - i\,|\,\mathbf{q}-\boldsymbol{\varkappa}/2\,|$$
$$+\widetilde{\Gamma}_{\mathbf{q}}(s + i\omega_0 + i\mathbf{qv}_p)/2]^{-1}.$$

The sum over $\mathbf{q}$ is here replaced by an integral and $\mathbf{k}$ denotes a unit vector in the direction of $\mathbf{q}$.

The integrand is a sharp function of the variable q with a maximum near the point $q = \omega_0$. We can thus replace $\mathbf{q}$ by $\omega_0\mathbf{k}$ in the slowly varying factors, and also in the quantities $\Gamma_{\mathbf{q}}$, $\boldsymbol{\kappa}\cdot\mathbf{q}$, and $\mathbf{q}\cdot\mathbf{v}_{\mathbf{p}}$. Moreover, since $\omega_0 \ll p_0$, we can replace the function $n_{\mathbf{p}-\mathbf{q}}$ by $n_{\mathbf{p}}$. The integral over the modulus of q can then easily be evaluated and we obtain for W_2 the expression (as $s \to 0$)

$$W_2 = \gamma\frac{1}{V}\frac{n_p}{2\pi}\int d\Omega\,\frac{G_{mm'}^{m_1m_1'}(\omega_0\mathbf{k})}{i\varkappa\mathbf{k} + \mathscr{T}(\mathbf{kv}_p)}\,\delta(\mathbf{kv}_p - \mathbf{kv}_{p_1}). \quad (15)$$

Here

$$\mathscr{T}(\mathbf{kv}_p) = \operatorname{Re}\Gamma_{\mathbf{q}}(s - i\omega_0 - i\mathbf{qv}_p)|_{s\to 0}$$
$$= \int\frac{d^3\mathbf{p}'}{(2\pi)^3}\frac{n_{p'}}{2j_0+1}\,2\pi\delta(\mathbf{qv}_p - \mathbf{qv}_{p'})\sum_{m\mu}|\,C_{\mathbf{q}\lambda}^{m\mu}\,|^2.$$

Using Eqs. (8) and (11) and putting $\mathbf{q} = \omega_0\mathbf{k}$, we get

$$\mathscr{T}(\mathbf{kv}_p) = \pi^{3/2}\frac{n_0}{\omega_0^3 v_0}\exp\left[-\frac{(\mathbf{kv}_p)^2}{v_0^2}\right]\frac{2j_1+1}{2j_0+1}\gamma, \quad (16)$$

where $v_0 = p_0/M$ is the most probable speed of the atom, j_1 and j_0 are the total angular momenta of the upper and lower levels. Thus, $W_{mm'}^{m_1m_1'}$ consists of two terms defined by Eqs. (11) ("departure" term) and (15) ("arrival" term).

Multiplying Eq. (10) by $s + i(\epsilon_{\mathbf{p}+\kappa/2} - \epsilon_{\mathbf{p}-\kappa/2}) = s + i\kappa\cdot\mathbf{v}_{\mathbf{p}}$ and changing to a coordinate-time representation, we get

$$\frac{\partial f_{mm'}(\mathbf{r},\mathbf{p},t)}{\partial t} + \mathbf{v}_p\nabla f_{mm'}(\mathbf{r},\mathbf{p},t) = -\gamma f_{mm'}(\mathbf{r},\mathbf{p},t)$$
$$+\gamma\int d^3\mathbf{p}'\int d^3\mathbf{r}'\sum_{m_1m_1'} K_{mm'}^{m_1m_1'}(\mathbf{r}-\mathbf{r}',\mathbf{p},\mathbf{p}')\,f_{m_1m_1'}(\mathbf{r}',\mathbf{p}',t)$$
$$+F_{mm'}(\mathbf{r},\mathbf{p},t). \quad (17)$$

Here

$$K_{mm'}^{m_1m_1'}(\mathbf{r},\mathbf{p},\mathbf{p}') = \frac{n_p}{(2\pi)^3}\int\frac{d\Omega}{(2\pi)^1}G_{mm'}^{m_1m_1'}(\omega_0\mathbf{k})$$
$$\times\int d^3\varkappa\,\frac{e^{i\varkappa\mathbf{r}}\delta(\mathbf{kv}_p - \mathbf{kv}_{p_1})}{i\varkappa\mathbf{k} + \mathscr{T}(\mathbf{kv}_p)}, \quad (18)$$

$F_{mm'}(\mathbf{r},\mathbf{p},t)$ describes the excitation of the atoms by the external field. For the case when the excitation is caused by light having a wide spectral composition the quantity $F_{mm'}(\mathbf{r},\mathbf{p},t)$ has been calculated before.[4] We changed in Eq. (17) for a summation over momenta to an integration, using the substitution

$$\frac{1}{V}\sum_{\mathbf{p}} \to \int\frac{d^3\mathbf{p}}{(2\pi)^3}.$$

We can evaluate the integrals in Eq. (18) using the identity

$$\int d\Omega\,\frac{\Phi(\mathbf{k})}{i\varkappa\mathbf{k} + \mathscr{T}(\mathbf{kv}_p)} = \int\frac{d^3\boldsymbol{\rho}}{\rho^2}\,e^{-\rho\mathscr{T}(\mathbf{kv}_p)}\,e^{i\varkappa\rho}\Phi(\mathbf{k}).$$

We have introduced here the vector $\boldsymbol{\rho} = \rho\mathbf{k}$. The integration over $\boldsymbol{\kappa}$ gives then a δ-function and we get

$$K_{mm'}^{m_1m_1'}(\mathbf{r},\mathbf{p},\mathbf{p}') = \frac{n_p}{(2\pi)^3}\frac{1}{2\pi\,|\,\mathbf{r}\,|^2}G_{mm'}^{m_1m_1'}(\omega_0\mathbf{n})$$
$$\times\delta(\mathbf{nv}_p - \mathbf{nv}_{p'})\exp(-\mathscr{T}(\mathbf{nv}_p)\,|\mathbf{r}|). \quad (19)$$

Here $\mathbf{n}$ is a unit vector in the direction of $\mathbf{r}$.

Equation (17) with the kernel (19) is a kinetic equation for the off-diagonal density matrix of the excited atoms. It changes into the usual equation for the diffusion of radiation [8], if we bear in mind that $f_{mm'} = \delta_{mm'}f$ and take the trace with respect to the magnetic quantum numbers of the equation. The term $v_p\nabla f_{mm'}$ can be dropped if the atom traverses during the time of the emission, a distance small compared to the characteristic length over which $f_{mm'}$ changes.

3. SOLUTION OF THE KINETIC EQUATION FOR AN UNBOUNDED MEDIUM

If the medium is unbounded and the excitation uniform, $f_{mm'}$ will be independent of the coordinate. We can then in Eq. (17) in the second term on the right integrate over $\mathbf{r}'$. It follows from Eq. (19) that

$$\int K_{mm'}^{m_1m_1'}(\mathbf{r},\mathbf{p},\mathbf{p}')\,d^3\mathbf{r}$$
$$= \frac{n_p}{(2\pi)^3}\frac{1}{2\pi}\int d\Omega\, G_{mm'}^{m_1m_1'}(\omega_0\mathbf{n})\,\frac{\delta(\mathbf{nv}_p - \mathbf{nv}_{p'})}{\mathscr{T}(\mathbf{nv}_p)}. \quad (20)$$

We shall assume that $F_{mm'}(\mathbf{r},\mathbf{p},t) = n_p(2\pi)^{-3}F_{mm'}(t)$, i.e., that the excited atoms are created with a Maxwellian momentum distribution. This is valid for excitations by electron collisions or for excitations by light of which the spectral width is larger than the Doppler line width of the excited gas. One can verify then that the function $f_{mm'}$ can be looked for in the form

$$f_{mm'} = (2\pi)^{-3}n_p f_{mm'}(t), \quad (21)$$

i.e., in the given case, the distribution of the excited atoms over the momenta remains for all times a Maxwellian one.

Indeed, we substitute (21) in (17) and integrate over the momenta $\mathbf{p}'$ using (20) and (16). It then turns out that each term in the equation contains a factor $(2\pi)^{-3}n_p$. Dividing by that factor, we get

$$\frac{df_{mm'}(t)}{dt} = -\gamma f_{mm'} + \gamma \sum_{m_1m_1'} g_{mm'}^{m_1m_1'} f_{m_1m_1'} + F_{mm'}(t), \quad (22)$$

$$g_{mm'}^{m_1m_1'} = \frac{3}{(2\pi)^3}\frac{2j_0+1}{2j_1+1}\frac{1}{d^2}\int d\Omega G_{mm'}^{m_1m_1'}(\omega_0\mathbf{n}). \quad (23)$$

After summing in Eq. (14) over the polarizations and integrating over the angles, the matrix g becomes

$$g_{mm'}^{m_1m_1'} = \frac{3}{10}\frac{1}{d^4(2j_1+1)}\sum_{\mu\mu'}\{(\mathbf{d}_{m_1\mu'}^*\mathbf{d}_{m_1'\mu})(\mathbf{d}_{m\mu}\mathbf{d}_{m'\mu}^*)$$
$$+ 6(\mathbf{d}_{m_1\mu'}^*\mathbf{d}_{m\mu})(\mathbf{d}_{m_1'\mu_1}\mathbf{d}_{m'\mu}^*) + (\mathbf{d}_{m_1\mu'}^*\mathbf{d}_{m'\mu}^*)(\mathbf{d}_{m\mu}\mathbf{d}_{m_1'\mu'})\}. \quad (24)$$

For the case $j_1 = 1$, $j_0 = 0$, for instance,

$$g_{mm'}^{m_1m_1'} = \frac{1}{10}(\delta_{m_1m_1'}\delta_{mm'} + 6\delta_{m_1m}\delta_{m_1'm'}$$
$$+ \delta_{m_1,-m'}\delta_{m,-m_1'}(-1)^{m+m'}).$$

Account of the diffusion of the radiation leads to the conclusion that the equations for different elements of the density matrix $f_{mm'}$ turn out to be coupled to one another. To solve the set (22) in the general case, it is convenient to expand the density matrix in terms of irreducible tensor operators [14]:

$$\hat{f} = \sum_{\varkappa=0}^{2j_1}\sum_{\alpha=-\varkappa}^{\varkappa}\hat{T}_{-\alpha}^{\varkappa}f_\alpha^\varkappa(-1)^\alpha; \qquad \mathrm{Sp}\,\hat{f} = f_0^0. \quad (25)$$

The T_α^κ operators are normalized such that

$$(T_\alpha^\varkappa)_{mm'} = \frac{2\varkappa+1}{(2j_1+1)^{1/2}}(-1)^{j_1-m'}\begin{pmatrix} j_1 & \varkappa & j_1 \\ -m & \alpha & m' \end{pmatrix}. \quad (26)$$

We have used here Wigner's 3j-symbol. Then

$$\sum_{mm'}(T_\alpha^\varkappa)_{mm'}(T_{\alpha_1}^{\varkappa_1})_{mm'} = \frac{2\varkappa+1}{2j_1+1}\delta_{\alpha\alpha_1}\delta_{\varkappa\varkappa_1}. \quad (27)$$

Using the orthogonality relation (27) one can easily express f_α^κ in terms of $f_{mm'}$:

$$f_\alpha^\varkappa = \frac{(-1)^\alpha(2j_1+1)}{2\varkappa+1}\sum_{mm'}(T_{-\alpha}^\varkappa)_{mm'}f_{mm'}. \quad (28)$$

From the hermiticity of the matrix $f_{mm'}$ it follows that

$$(f_\alpha^\varkappa)^* = (-1)^\alpha f_{-\alpha}^\varkappa.$$

We can now find solutions of the set of Eqs. (22) for the quantities f_α^κ:

$$df_\alpha^\varkappa/dt = -\gamma_{\varkappa\infty}f_\alpha^\varkappa + F_\alpha^\varkappa(t), \quad (29)$$

$$F_\alpha^\varkappa(t) = (-1)^\alpha\frac{2j_1+1}{2\varkappa+1}\sum_{mm'}(T_{-\alpha}^\varkappa)_{mm'}F_{mm'}(t);$$

$$\gamma_{\varkappa\infty}/\gamma = 1 - A_\varkappa; \quad (30)$$

$$A_\varkappa = \frac{3}{10}(2j_1+1)[6+(-1)^\varkappa]\begin{Bmatrix} 1 & 1 & \varkappa \\ j_1 & j_1 & j_0 \end{Bmatrix}^2, \quad \varkappa \neq 0, \quad A_0 = 1,$$

so that $\gamma_{0\infty} = 0$. The expression within the braces is a 6j-symbol. When deriving Eqs. (27) and (28) we used the representation of the matrix elements of the dipole moment in terms of 3j-symbols and Eqs. (2.20), (2.21), and (4.17) from [14].

Equations (25) and (29) give us the complete solution of the given problem. If we put $F_\alpha^\kappa = 0$, these equations describe the decay of the off-diagonal elements and the equalization of the populations on the sublevels of the excited state. It follows from Eqs. (30) and the properties of the 6j-symbols that $\gamma_{\kappa\infty}$ differs from γ only when $\kappa = 1$ and $\kappa = 2$ so that there are two relaxation times differing from the natural lifetime.

Using the formulae for the evaluation of the 6j-symbols [14] we can find explicit expressions for $\gamma_{1\infty}$ and $\gamma_{2\infty}$:

$$\frac{\gamma_{1\infty}}{\gamma} = 1 - A_1 = 1 - \frac{1}{16}\frac{Y^2}{j_1(j_1+1)};$$

$$\frac{\gamma_{2\infty}}{\gamma} = 1 - A_2 = 1 - \frac{7}{100}\frac{\{3Y(Y-1)-8j_1(j_1+1)\}^2}{(2j_1-1)2j_1(2j_1+2)(2j_1+3)}, \quad (31)$$

where $Y = (j_1 - j_0)(j_1 + j_0 + 1) + 2$.

We note that the intensity of the emission of light which is linearly polarized, for instance, along the z axis, is proportional to the expression

$$\sum_{mm'\mu} f_{mm'}d_{m\mu}^z(d_{m'\mu}^*)^z,$$

which can easily be shown to contain only f_α^κ for $\kappa = 0$ and $\kappa = 2$. In experiments in which the degree of linear polarization of the emitted light is measured the quantity $\gamma_{2\infty}$ will thus appear.

If we bear in mind that when the excitation is by light [4]

$$F_{mm'} \sim \sum_\mu(\mathbf{d}_{m\mu}\mathbf{E})(\mathbf{d}_{m'\mu}^*\mathbf{E}^*) \quad (32)$$

(where $\mathbf{E}$ is the complex amplitude of the electrical field in the exciting light) we can use Eq. (30) to reach the conclusion that when the excitation is by plane polarized or unpolarized light only the f_α^κ with $\kappa = 2$ or $\kappa = 0$ are excited, i.e., there is one relaxation time $\gamma_{2\infty}^{-1}$. Barrat [7] evaluated the quantity $\gamma_{2\infty}^{-1}$. The values obtained from Eq. (31) agree with his results.

The second relaxation time $\gamma_{1\infty}^{-1}$ appears under radiation of circularly polarized light. This conclusion follows from Eqs. (32) and (30) and also from the fact that, apart from a factor, f_{α}^{1} ($\alpha = 0, \pm 1$) is the same as the average value of the vector of the magnetic moment of the excited state. One can say that $\gamma_{1\infty}^{-1}$ is the time for the decay of the magnetic moment of the excited state.

If a magnetic field **H** is applied to the system, we must add to the Hamiltonian a term

$$V_3 = \mu_0 g \mathbf{HJ},$$

where $\mu_0 g$ is the gyromagnetic ratio, μ_0 the Bohr magneton, and **J** the operator of the angular momentum. We must then add to the right-hand sides of Eqs. (17) and (22) the term

$$-i[V_3, f]_{mm'} = -i\mu_0 g \mathbf{H} \sum_{m''} (\mathbf{J}_{mm''} f_{m''m'} - f_{mm''} \mathbf{J}_{m''m'}).$$

This obvious result can, of course, also be obtained by the diagram technique developed in Sec. 2. The other terms in Eqs. (17) and (22) remain unchanged, if we assume that the magnetic splitting is small compared with the Doppler line width and that the magnetic field varies little over a period equal to the reciprocal of the Doppler width.

To the right-hand side of Eq. (29) we must add a term

$$-i(-1)^{\alpha} \frac{2j_1+1}{2\varkappa+1} \sum_{mm'} (T_{-\alpha}^{\varkappa})_{mm'} [V_3, f]_{mm'}$$

$$= \frac{i\mu_0 g}{\sqrt{2}} \{\sqrt{(\varkappa+\alpha)(\varkappa-\alpha+1)} H_1 f_{\alpha-1}^{\varkappa} + \alpha\sqrt{2} H_0 f_{\alpha}^{\varkappa}$$

$$- \sqrt{(\varkappa-\alpha)(\varkappa+\alpha+1)} H_{-1} f_{\alpha+1}^{\varkappa}\}. \qquad (33)$$

It is clear that the equations for the f_{α}^{κ} with different κ remain independent also when there is a magnetic field. The discussion given above about the occurrence of the relaxation times $\gamma_{1\infty}^{-1}$ and $\gamma_{2\infty}^{-1}$ remains thus valid. In double resonance experiments [2], experiments on the magnetic depolarization of light [1], paramagnetic resonance experiments [4], and so on, the relaxation time $\gamma_{2\infty}^{-1}$ will occur. In experiments in which one can observe the relaxation of the magnetic moment of the excited state, the time $\gamma_{1\infty}^{-1}$ will occur. We note that Eq. (29) with expression (33) added to its right-hand side is, in fact, for $\kappa = 1$ the Bloch equation for the magnetic moment in cyclic components.

4. RADIATION DIFFUSION IN A FINITE MEDIUM

When the volume is finite, Eq. (17) is very complex. The equations for the f_{α}^{κ} with different κ will, generally speaking, not separate and it is thus impossible to state that in experiments on the magnetic depolarization of light (Hanle effect) the line retains a Doppler shape. A detailed description of the effect depends on the shape of the volume and the distribution of the excitation intensity over the volume. We note that the already mentioned specific diffusion of radiation does not make it possible to change from an integral equation to the differential equation of diffusion.

To obtain a qualitative description of the influence of the finite dimensions of the vessel, we can proceed as follows. We shall assume that the momentum distribution of the excited atoms is Maxwellian. We integrate Eq. (17) over the momenta and average it over the coordinates. We replace, moreover, in the integral term in Eq. (17) the function $f_{mm'}$ by its average value and the quantity $V^{-1}\int d^3r \int d^3r' K(r - r')$ by $\int d^3\rho K(\rho)$. After changing to the variables f_{α}^{κ} we then get instead of Eq. (29)

$$\frac{df_{\alpha}^{\varkappa}}{dt} = -\gamma_{\varkappa} f_{\alpha}^{\varkappa} + F_{\alpha}^{\varkappa}; \qquad (34)$$

$$\gamma_{\varkappa}/\gamma = 1 - A_{\varkappa} x, \qquad (35)$$

$A_0 = 1$, and A_1 and A_2 are determined by Eqs. (31);

$$x = 1 - \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} \exp\left\{-\frac{L}{l_0} e^{-t^2}\right\} dt,$$

$$l_0 = \frac{2j_0+1}{2j_1+1} \frac{8\pi^{3/2} v_0}{n_0 \lambda^3 \gamma} \qquad (36)$$

is a quantity which has the meaning of the mean free path of a photon in the center of the line, L a characteristic dimension of the vessel. The integral occurring in Eq. (36) is tabulated in [1]. When $L/l_0 \gg 1$

$$1 - x \approx \frac{l_0}{L}\left(\pi \ln \frac{L}{l_0}\right)^{-1/2}.$$

When $\kappa = 0, 2$ Eq. (35) is similar to the result obtained by Barrat. The method applied by us to estimate the relaxation time for a finite volume is essentially equivalent to Barrat's method. Our result differs, however, essentially from his result in that Barrat assumed that all atoms had the same speed. In the single-speed approximation, the mean free path of the photon is important, while it is impossible to introduce such a quantity for a Maxwell distribution, [8, 10] and the attenuation of the beam of light is not exponential. In accordance with this we obtain instead of Barrat's result $\gamma_0 \approx \gamma \exp[-\sqrt{(\pi/6)}\, L/l_0]$ for the reciprocal of the de-excitation time the estimate

$$\gamma_0 \approx \gamma \frac{l_0}{L}\left(\pi \ln \frac{L}{l_0}\right)^{-1/2}.$$

Apart from a factor of order unity, this estimate agrees with the result of the more detailed calculation by Holstein.[8]

The quantities γ_1 and γ_2 approach their limiting values considerably more slowly than exponentially when the pressure is increased. This agrees with the experimental data on γ_2 [6] and on the degree of polarization.[15] As far as we know, the quantity γ_1 has not been measured. We can obtain a more exact estimate of the relaxation time for a finite volume by using the variational method developed by Holstein to determine γ_0. For instance, when $j_0 = 1$, $j_1 = 0$ we can obtain by such a method for a plane lamina of thickness $2L (L \gg l_0)$

$$\gamma_2 = \left(1 - \frac{7}{10} x_2\right)\gamma, \quad x_2 = 1 - \frac{75}{64}\frac{l_0}{L}\left(\pi \ln \frac{L}{l_0}\right)^{-1/2}.$$

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